Electrophotographic Positively Charged Toner and Manufacturing Method Thereof

Cross Reference to Related Application

This application claims foreign priority of Japanese Patent Application Serial Nos. JP PA 2003-350356 and JP PA 2002-345636, the full disclosures of which are incorporated herein by reference.

Background of the Invention

1.Field of the Invention

The invention relates to an electrostatic latent image toner that can be used in an electrophotographic type image forming apparatus, and in particular to an electrophotographic positively charged toner, and a method of manufacturing it.

2. Description of the Related Art

When developing electrostatic latent images used in electrostatic copiers, printers and so on that use an electrophotographic method, toner is conveyed and attached to an electrostatic latent image on the surface of a photoreceptor. The photoreceptor has been formed through previous charging and exposure steps, whereby the image is made visible. The toner image is transferred from the surface of the photoreceptor onto a transfer medium (paper etc.) in a subsequent transfer step. It is then fused in a fusing step, before the transfer medium (paper, etc.) is discharged with the image printed thereon as a printed image. In general, the developing step can be broadly classified into a two-component developing method in which a toner and a carrier are used in combination, or a one-component

developing method in which a toner is used alone.

The toners used in these developing methods are generally obtained by first dispersing carbon black, a pigment or the like as a colorant through hot melt-kneading in a binder resin comprising a thermoplastic resin such as a natural resin. The hot melt-kneaded material is dry pulverized into fine particles. For example, the colorant may be dispersed by kneading in a binder resin having a styrene-acrylic copolymer as a principal component using an agitator such as a kneader, an extruder or a Banbury mixer, and then the kneaded material is fine pulverized into particles of size approximately 5 to 20μm to obtain the toner. Moreover, a magnetic toner can be obtained by further including a magnetic powder, such as magnetite, when carrying out the kneading and dispersion.

Toners used in the above-mentioned developing methods must in all cases be given a charge of positive or negative polarity corresponding to the polarity of the positive or negative charge on the surface of the photoreceptor before the formation of the electrostatic latent image, and this charge must be maintained. To bestow the charge, it is possible to use the tribo-charging ability inherent to a material such as a binder resin or a colorant that is a constituent component of the toner.

However, in general the amount of charge obtained through the tribo-charging ability inherent to such a material is often too low for good image formation. Therefore, an image developed using only this tribo-charging is prone to indistinctiveness, with, for example, an observable background fog. Consequently, in actual practice, to give a toner the necessary tribo-charging ability for good image formation, in general a substance called a charge control agent, such as a dye, a

pigment or a specially synthesized organic compound, that makes it easy to bestow chargeability, is specially added. As such charge control agents, there are materials that provide a charge bestowing ability of positive polarity and those that bestow a negative polarity, with various materials being known for each.

Of these, as positive charge control agents, colorants such as various azine compounds, nigrosine dyes, triphenylmethane dyes and phthalocyanine pigments, and also quaternary ammonium salt compounds, and resins containing a quaternary ammonium salt group or an amine group, and so on are well known materials, and these have been widely used hitherto. Such charge control agents are usually used singly. Of these charge control agents, hitherto the nigrosine dye type positive charge control agents often have been used alone. However, because the chemical structure is complex, and chemical stability as a substance is poor, there has been a problem that chemical decomposition or degeneration is easily brought about through heat and mechanical shock due to friction during hot melt-kneading and so on. As a result, the charge stability is impaired and thus the charging ability drops. Therefore, the original charge bestowing ability of these charge control agents can no longer be exhibited.

Moreover, in the case of using a quaternary ammonium salt compound or a macromolecular compound (resin) containing a positively chargeable functional group such as a quaternary ammonium salt group or an amine group as a charge control agent, although problems during hot melt-kneading as in the case of the above-mentioned dyes do not occur, the tribo-charge bestowing ability is considerably lower than with the above-mentioned dyes. Hence, to obtain the

amount of charge required for good image formation using such a compound alone, the amount added of the charge control agent must be made high. However, with a resin type charge control agent as described above in particular, if the amount added is made too high, then there will be problems such as impairment of the offset resistance. Therefore, suitably adjusting the amount added is extremely difficult.

Details of the charge control agents described above are given in the following patent documents.

Japanese Patent Application Laid-open No. S62-210472

Japanese Patent Application Laid-open No. S63-60458

Japanese Patent Application Laid-open No. H3-80259

Japanese Patent Application Laid-open No. H5-119509

Japanese Patent Application Laid-open No. H11-242353

Japanese Patent Application Laid-open No. H11-242360

Japanese Patent Application Laid-open No. 2000-214633

Japanese Patent Application Laid-open No. 2001-92188

Moreover, in general, with styrene-acrylic copolymer resins and polyester resins that are widely used as binder resins, the tribo-charging polarity of the resin itself in the developing step is generally negative. Therefore, in the case of adjusting a toner to be positively charged overall through the action of an added positive charge control agent, the positive charge bestowing ability possessed by the toner may not necessarily be sufficient and stable as compared with the negative charge bestowing ability. For example, upon continuous printing, due to the charge

control agent gradually separating from the toner and so on, the toner is prone to a deterioration in charge. As a result, problems may arise such as image defects including printing density reduction and background fog. Moreover, a phenomenon of toner filming onto the photoreceptor may occur due to deterioration in charge. In this way, conventional toners, in particular positively charged toners having a charge control agent added thereto and obtained through dry pulverization, have been insufficient to maintain a prolonged ability to bestow a stable positive charge.

Furthermore, in recent years, to enable image quality to be improved with electrophotographic type copiers, printers and so on, there has been a transition to smaller particle sizes in toners used in such electrophotographic apparatuses. With the above-mentioned conventional dry pulverization method, upon a decrease in particle size, there are problems such as dropping fluidity and nonuniform chargeability, and accompanying this the image quality has deteriorated and the transfer efficiency has dropped. To resolve these problems, wet granulation methods that use emulsion polymerization or suspension of the binder resin have been developed. Further, toners with small particle size but without reduced fluidity have been obtained, and have already been practically implemented.

Objects and Summary of the Invention

However, with such wet granulation methods, impurities such as polymerization initiators and surfactants added during the granulation are prone to remaining in the toner particles after the granulation, which often has adverse effects on the chargeability, the insulation properties, etc. Furthermore, with the

above-mentioned wet polymerization granulation method, there is a limitation on what binder resins can be used, and hence the range of choices for selecting the resin is narrow. Furthermore, there are also other problems, such as limitations on the selection of the molecular weight distribution of the resin.

On the other hand, with the conventional dry pulverization method, a method is already known in which, after kneading, pulverization and classification, the toner is introduced into a hot air current, and the surfaces of the particles are melted to carry out spherification. By this method an attempt is made to resolve problems such as the above-mentioned drop in fluidity. However, a problem with this method is that upon carrying out the spherification by melting the surfaces of the toner particles the amount of charge on the toner drops. Specifically, through the melting of the surfaces of the toner particles, the charge control agent present and exposed at the surfaces is coagulated and coated by the molten resin, whereby the charging ability drops.

In view of the points described above, it is an object of the invention to provide a new electrophotographic positively charged toner and a manufacturing method thereof. The invention is such that even if after kneading, pulverization and classification the toner is made spherical by melting the surfaces of the particles in a hot air current and the charge control agent is not coated, and hence the toner's ability to charge is not reduced. Therefore, the toner has sufficient tribo-charging ability for good image formation, excellent transfer efficiency and excellent charge build-up performance, and also excellent charge stability during continuous printing.

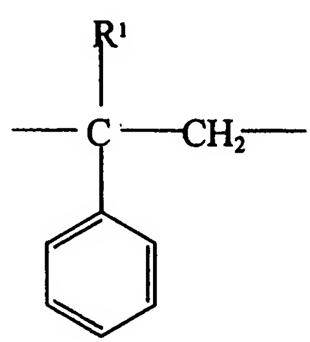
According to the invention, the above object is attained through an

electrophotographic positively charged toner comprising a core toner that has a binder resin, a wax, a colorant and a charge control agent as principal component materials, wherein the core toner has been spherified through heat treatment. The charge control agent contains both a resin having a quaternary ammonium salt group as a functional group, and a nigrosine dye. At least fine silica particles are provided as an external additive.

According to one aspect of the invention, the charge control agent of the electrophotographic positively charged toner preferably contains 2 to 10 parts by weight of the resin having a quaternary ammonium salt group as a functional group, and 0.5 to 5 parts by weight of the nigrosine dye, per 100 parts by weight of the binder resin.

According to another aspect of the invention, in the electrophotographic positively charged toner, the resin having a quaternary ammonium salt group as a functional group has as a principal component thereof a styrene-acrylic copolymer resin containing

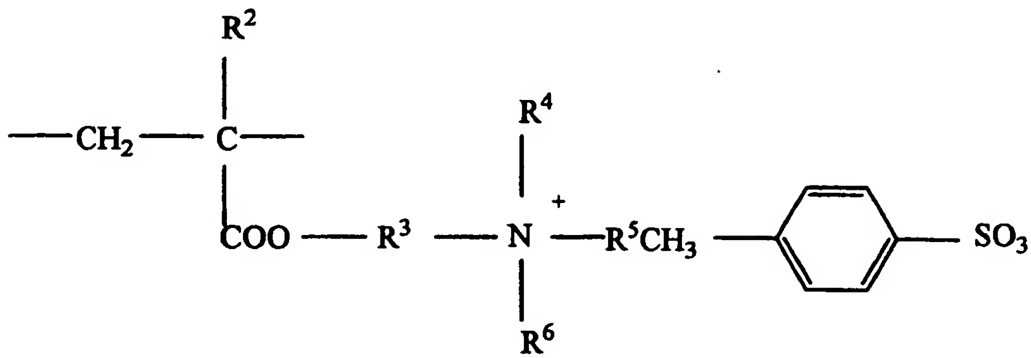
a repeat unit represented by the following formula (1)



(1)

and

a repeat unit represented by the following formula (2)



(2)

(where, in the formulae, R^1 and R^2 represent a hydrogen atom or a methyl group, R^3 represents an alkylene group, and R^4, R^5 and R^6 each represents an alkyl group, and the styrene-acrylic copolymer resin comprises 65 to 97 wt% of the repeat unit represented by formula (1) and 35 to 3 wt% of the repeat unit represented by formula (2), and has a weight average molecular weight in a range of 2,000 to 10,000).

According to the invention, the electrophotographic positively charged toner preferably is made to be such that the binder resin has a styrene-acrylic copolymer resin as a principal component thereof.

According to a still further aspect of the invention, the electrophotographic

positively charging toner is preferably made to contain 3 to 6 parts by weight of carbon black exhibiting a pH of at least 8.0 as the colorant per 100 parts by weight of the binder resin.

According to the invention, the above object is attained through a method of manufacturing the electrophotographic positively charging toner described above. The method includes mixing/agitating the binder resin, the wax, the colorant and the charge control agent, then hot melt-kneading, pulverizing and classifying the kneaded material obtained to produce a core toner, spherifying the core toner through hot air blast treatment, and then mixing in at least silica fine particles as an external additive.

According to the above-described toner and method of manufacturing, even if after kneading, pulverization and classification the toner is spherified by melting the surfaces of the particles in a hot air current, the charge control agent is not coated. Therefore, the charging ability of the toner is not reduced, and thus its tribo-charging ability is sufficient for good image formation, excellent transfer efficiency, and excellent charge build-up performance, and also the toner has excellent charge stability upon continuous printing.

Brief Description of the Drawings

Fig. 1 is a schematic sectional view of a spherifying apparatus for an electrophotographic positively charged toner according to the invention.

Fig. 2 is an SEM photograph of an electrophotographic positively charged toner before spherification.

Fig. 3 is an SEM photograph of the electrophotographic positively charged toner after spherification according to the invention.

Detailed Description of the Preferred Embodiments

Following is a detailed description of the electrophotographic positively charged toner of the invention, with reference to the drawings. The invention is not limited to the examples described below, provided the gist of the invention is not exceeded. Fig. 1 is a schematic sectional view of a treating apparatus for spherifying the electrophotographic positively charged toner according to the invention. Fig. 2 is an SEM photograph (800×) of the electrophotographic positively charged toner of the invention before the spherification. Fig. 3 is an SEM photograph (800×) of the electrophotographic positively charged toner after the spherification according to the invention.

The electrophotographic positively charged toner of the invention is obtained by a method that includes taking a binder resin, a wax, a colorant and a charge control agent as principal component materials, mixing/agitating these materials, then hot melt-kneading, pulverizing and classifying the kneaded material obtained, to obtain a core toner. The core tone is then spherified, and an external additive of silica fine particles is mixed in, etc. to further improve the fluidity of the toner. Following is a description of each of the above-mentioned materials, i.e. the binder resin, the wax, the colorant and the charge control agent in this order.

(Binder resin)

The binder resin used in the invention may be a resin having as a principal

component an ordinary thermoplastic resin having good fusing ability, hitherto well known as a binder resin. Examples are resins having as a principal component either a polyester resin, a polystyrene resin, a styrene-acrylic copolymer resin, an epoxy resin, a vinyl chloride resin, a vinyl acetate resin or the like, or a mixture of the above, or a copolymer resin of two or more of the above. In particular, if the charge control agent to be used according to the invention, to described later, has a styrene-acrylic copolymer resin as a base, a styrene-acrylic copolymer resin is preferable as the binder resin, since then compatibility is excellent, and hence there is an effect of preventing separation of the charge control agent upon repeated use of the toner being prevented. In the case of using a styrene-acrylic copolymer resin as the binder resin, for example, to obtain both good fusing ability and good offset resistance for the toner, it is preferable for the resin to exhibit a molecular weight distribution in a range of 2,000 to 900,000, with peaks at both a low molecular weight of several thousand and a high molecular weight of several hundred thousand.

(Wax)

The electrophotographic positively charged toner of the invention contains a wax for the purpose of improving the offset resistance. A publicly known wax such as polyethylene wax, polypropylene wax, beeswax or carnauba wax can be used. The amount of the wax preferably is in a range of 1 to 7 parts by weight per 100 parts by weight of the binder resin. At less than 1 part by weight, the offset resistance will be poor, and at more than 7 parts by weight, the toner particles are prone to coagulation.

(Colorant)

As the colorant in the electrophotographic positively charged toner of the invention, a single publicly known dye or pigment such as carbon black, lamp black or iron black, or a mixture thereof can be used. If the colorant is carbon, the amount used preferably is in a range of 3 to 6 parts by weight per 100 parts by weight of the binder resin.

It has been ascertained that if the carbon black used in the toner according to the invention is made to be alkaline with a pH of at least 8.0, then the polarity of tribo-charging will be positive. The pH of the carbon black is measured using a sludge thereof. The pH is affected primarily by the number of oxygen-containing groups on the surface of the carbon black, and by the amount of ash (metal oxides and other residues). It is known that in general channel black is acidic, and furnace black is neutral to alkaline.

(Charge control agent)

A resin having a quaternary ammonium salt group as a functional group and a nigrosine dye are used together as the charge control agent contained in the electrophotographic positively charged toner of the invention. As the resin, a positive charge control agent as described in detail in Japanese Patent Application Laid-open No. S63-60458 can be used. As described in Japanese Patent Application Laid-open No. S63-60458, the weight average molecular weight Mw of this resin (copolymer) is 2,000 to 10,000. If the weight average molecular weight Mw is less than 2,000, then the drop in the amount of charge in a high-temperature high-humidity environment will be large, and there is a tendency toward offset during

fusing. If the resin's weight average molecular weight Mw is more than 10,000, then its compatibility with the binder resin will be poor, and hence uniform dispersion will be difficult to obtain. In the invention, a weight average molecular weight Mw of 3,000 to 8,000 is preferred. Moreover, the viscosity of the above resin effects its ability to be kneaded with the binder resin and the fusing ability of the toner, and hence is preferably 50 to 10,000 poise, still more preferably 100 to 5,000 poise, at 130°C. The content of the above resin in the toner is preferably 2 to 10 parts by weight per 100 parts by weight of the binder resin. At less than 2 parts by weight, the amount of charge necessary for good image formation will be difficult to obtain, and thus severe toner clouding may occur. If the resin is more than 10 parts by weight, the toner is prone to experience problems such as a drop in environmental resistance, a drop in compatibility, and offset. Acrybase FCA-201-PS (trade name) made by Fujikura Kasei Co., Ltd., which is a resin having a charge control function, is preferred as the resin having a quaternary ammonium salt group as a functional group.

The nigrosine dye is a black dye, and is well known as a charge control agent. It is a mixture of azine compounds. The content (relative amount) of the nigrosine dye in the toner preferably is 0.5 to 5 parts by weight per 100 parts by weight of the binder resin. At less than 0.5 parts by weight, the amount of charge necessary for good image formation is difficult to obtain, whereas at more than 5 parts by weight, the toner is prone to loss of charge, and hence the amount of charge will be unstable. In addition to the principal component materials described above, i.e. the binder resin, the wax, the colorant and the charge control agent, a

small amount of a crystalline magnetic material may be added as required, for the purpose of increasing the hardness of the toner particles.

In addition to the above, a fatty acid-modified nigrosine dye, a metal-containing nigrosine dye, a metal-containing fatty acid-modified nigrosine dye, a salicylic acid chromium complex, a quaternary ammonium compound or the like can be used as a charge control agent.

(External additives)

As external additives in the invention, slip additives such as fine tetrafluoroethylene particles, zinc stearate and titanium oxide, abrasives such as cerium oxide and silicon carbide, fluidity bestowing agents such as hydrophobic silica, electrical conductivity bestowing agents such as carbon black and tin oxide, and so on may be added to the core toner as required. Spherification is carried out on the toner of the invention to improve the fluidity of the core toner as described earlier. However, for good image formation, further improvement in the fluidity is necessary. Therefore, at least hydrophobic silica is mixed in as an external additive for improving the fluidity.

(Examples)

Following is a detailed description of an electrophotographic positively charged toner, and a method for its manufacture, along with an evaluation, for several examples according to the invention and comparative examples not falling within the invention, showing how the toner of the invention is superior. In the

following description, 'parts' always means 'parts by weight'.

(Example 1)

(Binder resin)

Styrene / n-butyl acrylate copolymer resin

(CPR250, made by Mitsui Chemicals Inc.) 100 parts

(Wax)

Low-molecular-weight polypropylene

(Hiwax NP-055, made by Mitsui Chemicals Inc.) 5 parts

(Colorant)

Carbon black (Regal 330R, Cabot Corporation) 6 parts

(Charge control agent)

Nigrosine dye

(Bontron N-01, Orient Chemical Industries, Ltd.) 2 parts

Resin having quaternary ammonium salt group as functional group

(Acrybase FCA-201-PS, Fujikura Kasei Co., Ltd.) 3 parts

(Hiwax, Regal, Bontron and Acrybase are all registered trademarks.)

A combination of the above components was thoroughly mixed/agitated in a Henschel mixer, and was then subjected to hot melt-kneading in a twin-screw extruder; the kneaded material obtained was cooled down to room temperature, and then coarse pulverization, fine pulverization and classification were carried out, thus obtaining an unspherified black core toner having a mean volumetric particle size of

10 μm and a particle size distribution of 5 to 20 μm. An SEM photograph of the un-spherified core toner is shown in Fig. 2. It was found that the unspherified toner shown in Fig. 2, as is, had very poor fluidity. It was thought that this was due to the angular shape of the particles as shown in Fig. 2.

Following is a description of the method of spherifying the unspherified core toner. Fig. 1 shows a schematic sectional view of the spherifying apparatus for the electrophotographic positively charged toner according to the invention. Air 102, fed in from a blower 1, is introduced into a hot air blast generator 2, and creates a hot air blast 103 at 400°C and a flow rate of 0.2 to 0.3 m^3/min. The hot air blast 103 passes through an introducing pipe 2-1 and is fired into a first cyclone 7 from a hot air blast jetting nozzle 4. Meanwhile, the untreated core toner particles 10 are conveyed from a feeder 3 for a fixed amount of powder by a prescribed amount of high-pressure air 101 and are fed into a toner firing device 5, whereupon the untreated core toner particles 10 are jetted into the first cyclone 7 from a firing nozzle 6 by the pressure of the high-pressure air 101. The jetted core toner particles 10 instantaneously contact the hot air blast 103, the temperature of which has been adjusted as mentioned above, and are thus subjected to uniform heat treatment and hence are spherified. The core toner particles 10 that have been spherified by the heat treatment are immediately cooled by cooling air 104, and pass through an introducing pipe without becoming attached to an inner wall of the first cyclone 7, which is equipped with a cooling water circulating jacket 7-1, and without agglomerating. The cooled, spherified particles 10 then are fed into a second

cyclone 8 equipped with a cooling water circulating jacket 8-1, whereupon the spherified toner is further cooled, before being collected in a toner storage vessel 9. The cooling air 105 escapes from an opening in an upper part of the second cyclone 8 into a bag filter, not shown. An SEM photograph of the spherified toner collected from the spherifying apparatus is shown in Fig. 3. It can be seen from FIG. 3 that the particles of the spherified toner that has been subjected to the heat treatment have a spherical shape with no angular parts, and it was found that the fluidity of the toner was improved. However, even though the fluidity was improved, the fluidity was still not at the level required for good image formation.

According to the spherification of the toner of the invention, because a resin having a quaternary ammonium salt group as a functional group and a nigrosine dye are used together as the charge control agent, a problem that has occurred with conventional spherified toners does not occur. That is, the charge control agent according to the conventional spherified toners is taken into a binder resin whose surface has melted through the heat treatment during the spherification, and hence the charge control agent is coated, thus reducing the charge bestowing ability. To the contrary, with the toner of the invention, one component of the charge control agent is a resin, and this charge control agent resin is attached to and covers the surface of the binder resin that forms the core of the toner before the spherification. Thus, even upon the heat treatment during the spherification, the charge control agent resin melts first and coagulates to the binder resin. As a result, during this process the charge control agent resin still is at the outermost surface of the toner, and not coated by the binder resin. Therefore, the charge bestowing ability of the

charge control agent resin of toner according to the invention is strong and effective. In fact, long-term stabilization of the charge bestowing ability is obtained because the charge control agent resin is firmly fixed to the binder resin.

However, the ability possessed of the charge control agent resin to bestow charge is considerably lower than that of a nigrosine dye or the like. Therefore, considering that new problems will arise if a large amount of this resin is added alone, it was realized that using a nigrosine dye, which has a high charge bestowing ability, together with the charge control agent resin would result in good effects. The invention therefore combines these two substances.

0.5 parts of hydrophobic silica (NA50Y made by Nippon Aerosil Co., Ltd.) as an external additive for further increasing the fluidity of the toner was mixed with 100 parts of the spherified toner obtained through the spherification described above in a 20-liter Henschel mixer for 3 minutes at 1800 revs/min, thus carrying out an external additive treatment. The toner according to the invention thus obtained had a static bulk density of 0.45, and extremely high fluidity was obtained (see Table 1 below).

Next, 5 parts of the toner of the invention, and 100 parts of a silicone-resin-coated ferrite carrier having a mean particle size of approximately 60μm were mixed together with agitation, thus preparing a two-component developer. The amount of charge for this two-component developer was measured using a CF-100 blow-off device made by Toshiba Chemicals, which is a device for measuring an amount of charge. The measured amount of charge was 55μC/g. Moreover, the build-up time taken to reach this amount of charge was 3 seconds (see Table 1). Next, using this developer, continuous printing of 50,000 sheets was carried out in a

high-temperature high-humidity environment of 35°C and 85%RH using a printer equipped with a positively charging organic photoreceptor, and an evaluation was performed. Note that the replenishing toner used in this evaluation test was the same toner of the invention as that used in the above-mentioned developer.

(Examples 2 to 4)

Examples 2, 3 and 4 were made to be the same as Example 1, except that the amounts of the nigrosine dye and the resin having a quaternary ammonium salt group as a functional group in the charge control agent, were changed to more desirable combinations of contents within the following ranges:

2 to 10 parts by weight of the resin having a quaternary ammonium salt group as a functional group, and

0.5 to 5 parts by weight of the nigrosine dye per 100 parts by weight of the binder resin.

Specifically, the examples were respectively 0.6 parts and 2 parts, 3 parts and 5 parts, and 5 parts and 10 parts of the resin and nigrosine dye, per 100 parts of the binder resin.

(Example 5)

Example 5 was made to be the same as Example 1, except that the relative amount of the resin having a quaternary ammonium salt group as a functional group in the charge control agent was made to be outside the above range of the Examples 2-4.

(Example 6)

Example 6 was made to be the same as Example 1, except that the relative amount of the nigrosine dye in the charge control agent was made to be outside the above range of the Examples 2-4.

(Comparative Example 1)

Comparative Example 1 was made to be the same as Example 1, except that the spherification was not carried out.

(Comparative Example 2)

Comparative Example 2 was made to be the same as Example 3, except that the spherification was not carried out.

(Comparative Example 3)

Comparative Example 3 was made to be the same as Example 1, except that the resin having a quaternary ammonium salt group as a functional group was not used in the charge control agent.

(Comparative Example 4)

Comparative Example 4 was made to be the same as Example 1, except that the nigrosine dye was not used in the charge control agent.

Table 1

	Nigrosine dye (parts)	Charge control agent resin (parts)	Spherification	Static bulk density	Amount of charge (μC/g)		Charge build-up time (s)	
					Initial	After 50K sheets	Initial	After 50K sheets
Example 1	2	3	Yes	0.45	55	53	3	3
Example 2	0.6	2	Yes	0.44	51	50	4	5
Example 3	3	5	Yes	0.45	53	51	3	4
Example 4	5	10	Yes	0.42	48	47	4	3
Example 5	2	12	Yes	0.42	50	48	5	4
Example 6	0.3	5	Yes	0.44	45	43	6	5
Comparative Example 1	2	3	No	0.32	41	35	25	36
Comparative Example 2	3	5	No	0.30	43	31	29	39
Comparative Example 3	2	0	Yes	0.41	35	23	18	26
Comparative Example 4	0	3	Yes	0.44	32	21	19	30

Table 2

	Nigrosine dye (parts)	Charge control agent resin (parts)	Solid image density		Background fog density		Transfer efficiency	Evaluation
			Initial	After 50K sheets	Initial	After 50K sheets		
Example 1	2	3	1.38	1.39	0.06	0.07	98	good
Example 2	0.6	2	1.42	1.40	"	"	95	good
Example 3	3	5	1.40	1.39	"	"	97	good
Example 4	5	10	1.39	1.40	"	"	96	good
Example 5	2	12	1.15	1.38	0.08	0.10	93	fair
Example 6	0.3	5	0.93	1.30	0.10	0.11	95	fair
Comparative Example 1	2	3	1.25	1.10	0.18	0.25	75	poor
Comparative Example 2	3	5	1.28	1.09	0.15	0.27	71	poor
Comparative Example 3	2	0	1.10	0.98	0.11	0.23	81	poor
Comparative Example 4	0	3	1.10	0.95	0.10	0.24	83	poor

The results of the printing evaluation are shown in the above Tables 1 and 2. Considering first Example 1, it can be seen from these tables that even under the severe environmental conditions described above, including the continuous printing of 50,000 sheets, there was little change, from the beginning to the end of the printing, in either the toner properties, i.e. the amount of charge and the build-up time thereof, or the image quality, i.e. the image density of solid parts and the background fog density of non-image parts. Moreover, the transfer efficiency always was maintained at at least 95%. It therefore should be apparent that stable printing quality could be obtained.

For Examples 2 to 4, in which the combination of the contents of the charge control agents' components was changed as described above, after the printing of 50,000 sheets the static bulk density, which indicates the fluidity, was approximately as good as for Example 1. Moreover, regarding the other evaluation results that compare initial conditions to those after 50,000 sheets had been printed, again there was little change either in the toner properties, i.e. the amount of charge and the build-up time thereof, or in the image quality, i.e. the image density of solid parts and the background fog density of non-image parts. Further, the transfer efficiency was always maintained at at least 95%. Thus, again, stable printing quality could be obtained. For Examples 5 and 6, the evaluation results were not as good as for Examples 1 to 4, but an improvement can be seen in comparison with Comparative Examples 1 to 4, which are discussed below.

Regarding the evaluation results for Comparative Examples 1 to 4, from

Tables 1 and 2, it can be seen that initially the amount of charge was low, the charge build-up time was rather long, the solid image density was low, and the background fog density was high. Moreover, there were large changes from before to after the printing of 50,000 sheets, in the toner properties, i.e. the amount of charge and the build-up time thereof, and in the image quality, i.e. the image density of solid parts and the background fog density of non-image parts. Furthermore, the transfer efficiency was low. Thus, stable printing quality clearly was not obtained.

In the following examples, a description will be given regarding embodiments of the invention, according to which the binder resin of the electrophotographic positively charging toner of the invention has a styrene-acrylic copolymer resin as a principal component and the toner contain 3 to 6 parts by weight of carbon black that exhibits a pH of at least 8.0 as the colorant per 100 parts by weight of the binder resin. In the following description, ‘parts’ always means ‘parts by weight’.

(Example 7)

(Binder resin)

Styrene / n-butyl acrylate copolymer resin

(Dianal FB-1157, made by Mitsubishi Rayon Co., Ltd.) 100 parts

(Wax)

Low-molecular-weight polypropylene

(Hiwax NP-055, made by Mitsui Chemicals Inc.) 5 parts

(Colorant)

Carbon black

(Regal 330R, made by Cabot Corporation; pH 8.5) 4 parts

(Charge control agent)

Nigrosine dye

(Bontron N-01, made by Orient Chemical Industries, Ltd.) 1 part

Resin having quaternary ammonium salt group as functional group

(Acrybase FCA-201-PS, made by Fujikura Kasei Co., Ltd.) 4 parts

A mixed material of the above composition was thoroughly mixed/agitated in a Henschel mixer. It was then subjected to hot melt-kneading in a twin-screw extruder, and the kneaded material was cooled down to room temperature. Then, the cooled kneaded material was subjected to coarse pulverization, fine pulverization and classification to obtain a black core toner having a mean volumetric particle size of 10 μm and a particle size distribution of 5 to 20 μm. 0.5 parts of hydrophobic silica (NA50Y made by Nippon Aerosil Co., Ltd.) as an external additive for bestowing fluidity was mixed with 100 parts of the core toner obtained as described above, in a 20-liter Henschel mixer for 3 minutes at 2000 revs/min, thus carrying out an external additive treatment whereby a toner of the invention was obtained. Next, 5 parts of this toner of the invention, and 100 parts of a silicone-resin-coated ferrite carrier having a mean particle size of approximately 60μm were mixed together with agitation, thus preparing a two-component developer.

The amount of charge for this developer was measured to be 45.5μC/g (see Table 3 below), using the CF-100 blow-off device made by Toshiba Chemicals. Moreover, the build-up time to reach this amount of charge was 4 seconds (Table 3).

Next, continuous printing of 10,000 sheets was carried out in a high-temperature high-humidity environment of 35°C and 85%RH with a non-magnetic one-component developing type printer equipped with a positively charging organic photoreceptor, using the toner of the invention obtained through the external additive treatment described above. An evaluation then was carried out. Note that the replenishing toner used in this evaluation test was the same toner of the invention.

(Examples 8 to 10)

Examples 8, 9 and 10 were made to be the same as Example 7, except that the relative amount of the colorant carbon black was changed respectively to 3 parts, 5 parts and 6 parts per 100 parts of the binder resin, which are within the range specified above, but different from the amount in Example 7.

(Examples 11 to 13)

Examples 11, 12 and 13 were made to be the same as Example 7, except that the colorant carbon black was Raven 420 made by Columbia Chemical Company (pH 9), Raven 1020 made by Columbia Chemical Company (pH 8.3) or Black Pearls 880 made by Cabot Corporation (pH 8), all of which exhibit a pH of at least 8.0.

(Comparative Examples 5 to 7)

Comparative Examples 5, 6 and 7 were made to be the same as the invention's Example 7, except that the colorant carbon black was respectively Raven 8000 made by Columbia Chemical Company (pH 2.4), Black Pearls L made by

Cabot Corporation (pH 2.5) and Regal 400 made by Cabot Corporation (pH 4), which all exhibit a pH outside the range of the invention.

(Comparative Examples 8 to 10)

Comparative Examples 8, 9 and 10 were made to be the same as the invention's Example 7, except that the content of the colorant carbon black was made to be respectively 2 parts, 7 parts and 9 parts per 100 parts of the binder resin, which are outside the range specified above for Examples 7-13 according to different embodiments of the invention.

Table 3

	Carbon black	pH	Content (parts)	Amount of charge (μC/g)		Charge build-up time (s)		Solid image density		Background fog density		Overall evaluation
	----		-- ---	Initially	After 10,000 sheets	Initially	After 10,000 sheets	Initially	After 10,000 sheets	Initially	After 10,000 sheets	-- -- -
Example 7	Regal 330R	8.5	4	45.5	45.9	4	5	1.44	1.39	0.06	0.07	good
Example 8	"	"	3	42.4	39.1	5	7	1.37	1.37	"	"	good
Example 9	"	"	5	44.9	44.2	4	5	1.41	1.40	"	"	good
Example 10	"	"	6	43.8	43.9	4	5	1.42	1.39	0.07	0.08	good
Example 11	Raven 420	9.0	4	46.4	45.8	5	6	1.38	1.36	0.06	0.07	good
Example 12	Raven 1020	8.3	4	38.2	36.7	6	7	1.41	1.38	"	"	good
Example 13	Black Pearls 880	8.0	4	43.6	41.3	5	6	1.39	1.37	"	"	good
Comparative Example 5	Raven 8000	2.4	4	11.2	5.2	28	35	1.10	0.98	0.11	0.23	poor
Comparative Example 6	Black Pearls L	2.5	4	10.5	6.3	20	28	1.10	0.95	0.10	0.24	poor
Comparative Example 7	Regal 400	4.0	4	13.1	7.1	25	23	1.15	1.05	0.09	0.20	poor
Comparative Example 8	Regal 330R	8.5	2	22.1	20.3	11	19	0.76	0.68	0.07	0.22	poor
Comparative Example 9	"	"	7	29.8	24.3	13	18	1.25	1.18	0.10	0.83	poor
Comparative Example 10	"	"	9	10.8	4.8	20	24	0.93	0.85	0.10	0.34	poor

The results of a printing evaluation are provided in Table 3, which shows conditions before and after continuous printing of 10,000 sheets. From Table 3, it can be seen that for Example 7, even in the case of evaluation under the severe environmental conditions described above, there was after the printing little change in the toner properties, i.e. the amount of charge and the build-up time thereof, or in the image quality, i.e. the image density of solid parts and the background fog density of non-image parts. Thus, it can be seen that with the electrophotographic, positively charged toner of Example 7, stable printing quality was obtained. For Examples 8 to 10, in which the content of the carbon black was changed as described above and Examples 11 to 13, in which the carbon black was changed to ones of different pH as described above, the results were approximately as good as for Example 7. Moreover, regarding the other evaluation results, again it can be seen that there was little change after printing 10,000 sheets, either in the toner properties, i.e. the amount of charge and the build-up time thereof, or in the image quality, i.e. the image density of solid parts and the background fog density of non-image parts. Thus, stable printing quality was obtained.

On the other hand, regarding the evaluation results for Comparative Examples 5 to 10, from Table 3, it can be seen that initially the amount of charge was low, the charge build-up time was rather long, the solid image density was low, and the background fog density was rather high. Moreover, after printing 10,000 sheets there were large changes in the toner properties, i.e. the amount of charge and the build-up time thereof, and in the image quality, i.e. the image density of solid parts and the background fog density of non-image parts. Consequently, it is clear that a

stable printing quality was not obtained. From the above comparison between Examples 7 to 13 and Comparative Examples 5 to 10, it can be seen that it is preferable to make at least 8.0 the pH of the colorant in the electrophotographic positively charging toner of the invention, and make the content of the colorant 3 to 6 parts by weight per 100 parts by weight of the binder resin.

It will be understood by those skilled in the art to which this invention pertains that the above description of the preferred embodiments are susceptible to various modifications, changes and adaptations, and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims.